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Xenon Fluorides Show Potential as Fluorinating Agents

The problem:

To devise a straightforward method for the controlled addition of fluorine across an olefinic double bond. The method should also permit ready separation of the product from the reduced fluorinating agent at a high purity. Present methods using elemental fluorine or metal fluorides for fluorinating olefins have a number of disadvantages in that the reactions are somewhat difficult to carry out and are often accompanied by fluorine substitution, cleavage of the double bond, or both.

The solution:

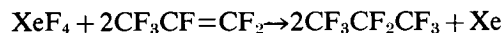
Xenon fluorides provide a series of fluorinating agents which appear attractive for controllable selective fluorinations yielding high purity products. They form elemental xenon as the only byproduct, and this is readily separable from the organic products. In addition, the reactions may be carried out in the vapor phase at room temperature, eliminating the problems associated with the use of solvents.

How it's done:

The use of xenon fluorides to effect fluorine addition to unsaturated organic molecules has been investigated at Argonne National Laboratory. The apparatus used in these investigations is similar to that used in the preparation of xenon fluorides, being constructed mainly of nickel or monel. Purified reactants were condensed at the temperature of liquid nitrogen (-195°) into a 130-cc nickel can which could be weighed. The can was allowed to warm to room temperature and the course of the reaction followed by observing the change of pressure in the can. It was assumed that the reaction had reached completion when no further pressure change was observed. The

reaction products were separated by trapping out components at differing temperatures and the various components were identified by their infrared, nuclear magnetic resonance, and/or mass spectra.

As an example of this type of reaction, 0.75 millimole of XeF_4 and 1.28 millimoles of perfluoropropene were allowed to stand in a nickel can at room temperature for 15 hours, after which the pressure was found to be constant. The mixture was cooled in a dry ice-trichloroethylene bath at -78° and the volatile material removed by pumping through a trap at -195° . The material collected was shown to contain only xenon and perfluoropropane, and the material remaining in the reaction vessel was found to be unreacted xenon tetrafluoride.



Under similar conditions XeF_6 , which is more reactive than XeF_4 , reacts with perfluoropropane to give both C_2F_6 and CF_4 as the major products. A mixture of XeF_2 , which is less reactive than XeF_4 , and perfluoropropene does not react even after 6 days. This suggests that XeF_2 is not an intermediate in these fluorinating reactions.

In additional investigations, it was shown that both xenon difluoride and xenon tetrafluoride react with ethylene at room temperature to give quantitative yields of 1:1 and 1:2 difluoroethane ($\text{CH}_2\text{FCH}_2\text{F}$) and elemental xenon.

Notes:

1. These investigations indicate that xenon fluorides have a considerable potential as fluorinating agents in organic chemistry, especially in small scale reactions where precise control and a high purity product are of importance.

(continued overleaf)

2. Additional details are contained in: *Journal of the American Chemical Society*, vol. 86, reference 5021 (1964).
3. Inquiries concerning this innovation may be directed to:

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Reference: B67-10185

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Patent status:

Inquiries about obtaining rights for commercial use of this innovation may be made to:

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